Fabrication and characterization of thin, self-supporting germanium single crystals

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Thin Ge single crystals (< 1 μm) up to 4 mm in diameter have been fabricated from epitaxial Ge films grown by atmospheric pressure chemical vapor deposition on Si(100) wafers. The thin Ge windows are formed by chemically etching away both the Si substrate and the region of the Ge film near the interface that contains misfit dislocations associated with heteroepitaxial growth and relaxation of the Ge films. The resulting Ge films are comparable in crystalline quality to bulk Ge wafers, as indicated by ion channeling studies.

INTRODUCTION

We shall describe in this article a detailed procedure for producing self-supporting Ge single crystals roughly 1 μm thick and 4 mm in diameter. The Ge windows are comparable in crystalline perfection to bulk Ge, as indicated by ion channeling. Although the use of self-supporting Ge crystals several μm thick has been reported in connection with nuclear physics experiments,[1] we believe no published literature describes their fabrication, uniformity or crystalline quality. Free-standing single-crystal Ge films fabricated by epitaxial growth onto NaCl and separation from the substrate by differential sheer stress have been reported,[2] but are substantially thicker (10 μm) than the films reported here. Thin Ge windows of high crystalline perfection may have applications including use in high angular resolution Compton gamma-ray telescopes[3] or infrared detectors. We are primarily interested in their application as substrates for surface studies using transmission ion channeling.[4]

EXPERIMENT

Using an Applied Materials 1200 epitaxy reactor at atmospheric pressure, epitaxial Ge layers with thicknesses of 0.5 – 4 μm were grown at Spire Corporation on clean Si(100). To produce clean surfaces, factory wafers were heated to 1200 °C for $\frac{1}{2}$ h and then etched *in situ* by passing HCl over the surface until approximately 1 μm of the Si was removed. Germanium tetrachloride ($GeCl_4$) was used as a Ge source. The growth rate ranged between 0.5 and 1.0 μm/min and growth temperatures from 750 to 850 °C. Transmission electron microscopy (TEM) and cross-sectional TEM (XTEM) were used to determine defect densities in the layers. A typical XTEM micrograph of the as-grown Ge film is shown in Fig. 1. The micrograph shows a defective region of misfit dislocations extending from the Ge/Si interface 2000–3000 Å toward the surface. A region of high crystalline quality extends about 5000 Å from the surface. A plan-view TEM survey of a large area near the surface of the sample indicates a defect density in the range of $10^6/cm^2$.[5] This defect density, low for epitaxial Ge layers on Si(100), is attributed to a far higher dislocation glide velocity at the relatively elevated growth temperatures employed in CVD.[6,7]

In order to produce thin windows several etching steps are applied to the as-grown samples. First, the samples are cleaved into 1.3 cm by 1.3 cm squares, and the front (Ge) and back (Si) of the sample are completely masked in Parafilm[8] except for a small ($\simeq 2$ mm) hole in the center of the back. A bath consisting of $HF:HNO_3:CH_3CO_2H$ (2:4:1 volumetric ratio) is then used to etch the unprotected region to a thickness ranging from a few to tens of microns. The length of time required in this etch bath to reduce a 400 μm wafer to a few microns is $\simeq 25$ min. The Parafilm is then removed, and the sample is submerged in a solution consisting of ethylenediamine:H_2O:pyrocatechol (EDP) in the ratio 50 ml:25 ml:10 g, held at 85 °C, which etches Si at a rate of 50 μm/h but etches Ge at a negligible rate. This part of the sample preparation is similar to that applied in the selective etching of doped Si for the production of thin Si windows as first described by Cheung.[9] Our experience indicates that further etching with KOH increases the window size more quickly and gently than continued etching in the EDP, so the samples are removed from the EDP just after the interface is reached and are placed in a 10 Normal solution of KOH at 85 °C until they are of suitable diameter. After these steps, the sample consists of a uniformly thin Ge window backed by a defect-ridden region and surrounded by a thick Si frame. The defective region is removed from the back of the window by masking the front of the sample in Parafilm (without contacting the thin part) and dipping it briefly ($\simeq 6$ s) in a mixture of HNO_3:HF (20:1 volumetric ratio).

Ion beam analysis was carried out in a high vacuum (10^{-6} Torr) ion scattering chamber connected to a 4.0 MeV Van de Graaff accelerator and equipped with a goni-

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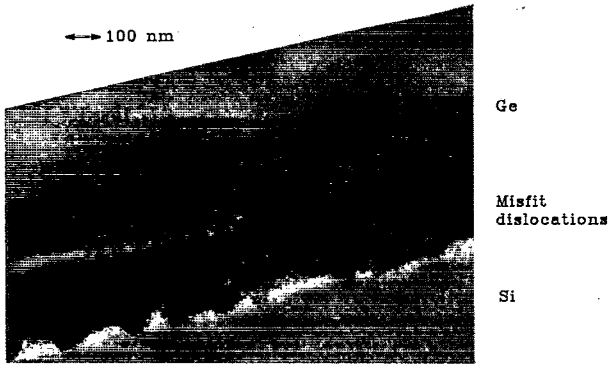

FIG. 1. XTEM of epitaxial Ge thin film on Si substrate grown by APCVD.

ometer having two stepper-motor-controlled angular degrees of freedom. For the data presented here, the beam was 2.0 MeV He^{+} and a surface barrier detector was placed at a scattering angle of 170°.

ION CHANNELING ANALYSIS OF AS-GROWN FILMS

Figure 2 shows ion scattering spectra for random (solid squares) and channeling (open circles) incidence of an as-grown 1.2 μm Ge film. The curves through the data points will guide the eye. The measured channeling spectrum for a bulk Ge crystal is also shown (dashed curve). The crystalline quality of the Ge epilayer is clearly indistinguishable from that of the bulk crystal in the region near the Ge surface. The peak in the channeling spectrum near 0.95 MeV is the result of ion beam dechanneling by defects in the Ge epilayer near the Si-Ge interface,[10] as well as direct scattering of the ion beam by the distorted channels

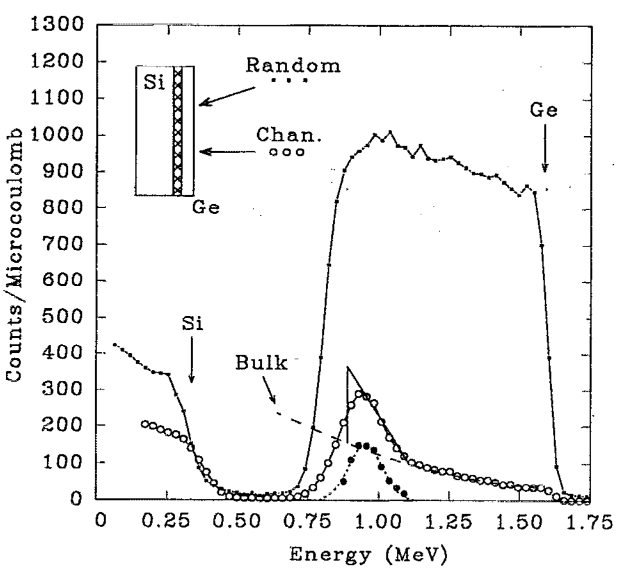

FIG. 2. Channeling and random spectra of as-grown Ge/Si(100). Also shown is the difference (solid circles) of the epitaxial Ge channeling spectrum (open circles) and the measured bulk Ge channeling spectrum (dashed line). A simple model for defect-induced dechanneling, assuming a constant dechanneling rate, is represented by the solid line.

near defects.[11] For the present case, we assume that the contribution from direct scattering is negligible compared to that from dechanneling.[10] Subtracting the bulk channeling curve from the channeling spectrum of the as-grown film isolates the dechanneling contribution of the defects (solid circles). This dechanneling peak has been fitted to a Gaussian function (dotted line). As a first approximation, we treat the defect-induced dechanneling rate near the interface as a constant. This gives rise to a linear increase in the channeling yield that is abruptly terminated by the end of the Ge epilayer. This abrupt fall is softened by the finite system resolution (including straggling) at the interface, yielding an interface peak. The onset of dechanneling was taken to be 1.11 MeV, coincident with the rise in the dechanneling peak, and the falling edge was set to 0.89 MeV, the half-height of the back edge of the dechanneling peak. This range of energies corresponds to a thickness of $\simeq$4000 Å in the Ge (or roughly $\frac{1}{3}$ of the Ge film), which implies that either the defects themselves, or the lattice distortions associated with them, are distributed over this range. A region containing lattice distortions over roughly $\frac{1}{3}$ of the Ge film is consistent with results from XTEM (Fig. 1).

The area of the triangular-shaped region (solid curve) was set equal to the area of the dechanneling peak, which determined the height of the triangle and, thus, the total fraction of the beam dechanneled by defects in the Ge film. Adding the contribution to the dechanneled fraction at the exit of the Ge film from the bulk crystal, 0.18, to the contribution from the defects, 0.20, yields a dechanneled fraction of 0.38 as the beam reaches the Si substrate. The minimum yield at a depth of 4000 Å into the Si substrate is 0.58. This implies (neglecting the dechanneling contribution from defect-free Si) that dechanneling from defects in the Si contributes 0.20 to the minimum yield, the same contribution as from dechanneling in Ge.

For a fully relaxed Ge film, the number of misfit dislocations at the interface can be calculated to be $N_d=0.02/$Å, assuming the Burger's vector lies in the interface plane.[10] Setting the dechanneling probability, $P=\sigma_d N_d$ equal to the dechanneling in the Ge film (0.20) gives an experimental value for the dechanneling cross section, $\sigma_d=10$ Å. A simple model for axial dechanneling by dislocations due to Quéré[12] gives a value for σ_d of 47 Å. However, a more rigorous computer calculation by Kudo[13] gives values for the dechanneling cross sections a factor of $0.2-0.7$ smaller than Quéré's for comparable systems. Thus, our data are consistent with dechanneling by misfit dislocations in a fully relaxed Ge film.

ION CHANNELING ANALYSIS OF THIN Ge WINDOWS

Figure 3 shows a channeling spectrum for a 1.2 μm Ge epilayer on Si exposed to the etching procedure described above, including the removal of the defective region (solid circles). Channeling spectra of the unetched sample (open circles) and of bulk Ge (dashed curve) are shown for comparison. This etching process removes the Si substrate and the defective region of the Ge epilayer. The Ge minimum yield on the window is clearly as low as that in the unetched region, and as low as that for bulk Ge. Channel-

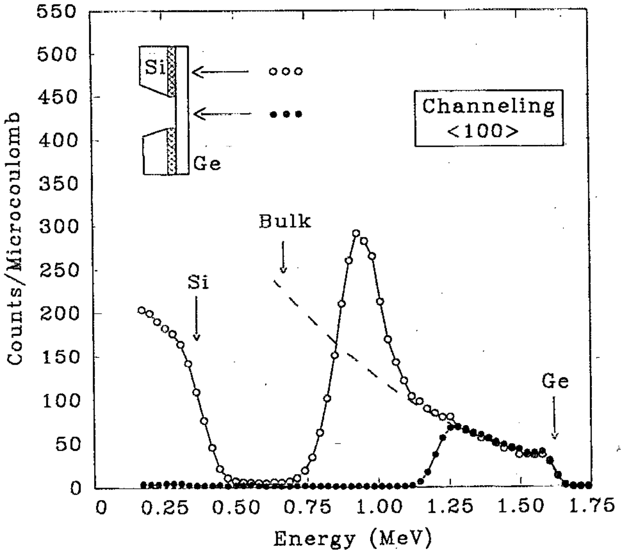

FIG. 3. Channeling spectra from an as-grown Ge/Si(100) film (open circles), from a self-supported thin Ge window with the defective region removed (solid circles), and from bulk Ge (dashed line).

ing spectra through the window have also been taken with the beam entering through the back (etched side) of the Ge and are indistinguishable from that shown in Fig. 3. This indicates that the crystalline quality of the window at the back is comparable to that at the front. A random spectrum from the window (not shown) has been used to estimate the thickness variation of the window over an area the size of the beam spot (1 mm^2). The falling edge of the random spectrum is broadened by contributions from a finite detector resolution, energy straggling through the sample, and nonuniform sample thickness. Treating the contribution from straggling with the Bohr theory, as outlined in Ref. 14, and taking the detector resolution from the rising edge of the random spectrum, we calculate the thickness variation of the window to be under 8%.

APPLICATION OF Ge WINDOWS FOR SURFACE STUDIES

We have recently shown that transmission ion channeling can be used to determine the bonding site of adsorbed atoms on the Si(100) surface.[4] Transmission channeling requires thin ($\leqslant 1\ \mu m$), high-quality single crystals, and surface structure studies require that the thin crystals can be rendered atomically clean and well-ordered in ultrahigh vacuum. We have found that a Ge window exposed to a channeled 2 MeV He ion dose of 42 $\mu C/mm^2$ shows no degradation in crystalline quality. A typical dose required for an energy spectrum is 6 to 12 μC. We have successfully sputter cleaned the thin Ge windows using 1.5 keV Ar bombardment to O levels below 0.4% and C below 0.3%, as determined by Auger electron spectroscopy. The sputtered samples have been annealed at approximately 600 °C to yield a sharp 2×1 low energy electron diffraction pattern with low background.

CONCLUSION

We have successfully fabricated thin, self-supporting Ge single crystals. The thin crystals are shown to be of high crystalline quality by ion channeling.

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